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Hydrous Ruthenium Oxide Nanoparticles Anchored to Graphene and Carbon Nanotube Hybrid Foam for Supercapacitors

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Abstract

In real life applications, supercapacitors (SCs) often can only be used as part of a hybrid system together with other high energy storage devices due to their relatively lower energy density in comparison to other types of energy storage devices, such as batteries and fuel cells. Increasing the energy density of SCs will have a huge impact on the development of future energy storage devices by broadening the area of application for SCs. Here, we report a simple

and scalable way of preparing a three-dimensional (3D) sub-5 nm hydrous ruthenium oxide (RuO₂) anchored graphene and CNT hybrid foam (RGM) architecture for high-performance supercapacitor electrodes. This RGM architecture demonstrates a novel graphene foam conformally covered with hybrid networks of RuO₂ nanoparticles and anchored CNTs. SCs based on RGM show superior gravimetric and per-area capacitive performance (specific capacitance: 502.78 F g⁻¹, areal capacitance: 1.11 F cm⁻²) at the same time which leads to a exceptionally high energy density of 39.28 Wh kg⁻¹ and power density of 128.01 kW kg⁻¹. The electrochemical stability, excellent capacitive performance, and the ease of preparation suggest this RGM system is promising for future energy storage applications.

Introduction

Among all energy storage devices, supercapacitors (SC) have garnered substantial attention in recent years due to their ultra-fast charge and discharge rate, excellent stability, long cycle life, as well as extremely high power density. These characteristics are desirable for many applications including electrical vehicles (EVs) and portable electronics^{1,2}. However, due to a relatively lower energy density in comparison to other types of energy storage devices such as batteries and fuel cells, in often cases SCs can only be used as part of a hybrid system with other high energy storage devices in real applications. Therefore, boosting the energy density of SCs has become one of the most promising methods for the development of future high energy and high power density energy storage devices. Energy density (E) is equal to $0.5CV^2$, where C is the specific capacitance and V is the operational voltage window. A boost in energy density can be achieved by increasing one or both of the specific capacitance and voltage windows. Moreover, power density is defined as $P=V^2/4R$, where $R=\rho L/A$. Here, R is equivalent series resistance

(*ESR*) of the SC and ρ , L , A are the specific electrical resistance, length of current flow, and area of current flow, respectively. Thus, high capacitance is critical to achieve higher energy density while large electrochemically accessible surface area, high electrical conductivity, short ion diffusion pathways, and excellent interfacial integrity are critical to achieve higher power density³. Additionally, both power density and energy density can be increased by the widening of the operational voltage window. Nanostructured active materials provide a mean to these ends and are crucial in fabricating high-performance SCs⁴⁻⁸.

There are two types of electrochemical capacitors: i) electrochemical double layer capacitors (EDLCs), which are generally based on pure graphitic nanostructures including CNTs, graphene, carbon onions/spheres, template derived carbons, activated carbon, etc^{4,9-14}. and ii) pseudocapacitors which are based on pseudocapacitive materials like V_2O_5 ^{15,16}, RuO_2 ¹⁷, MnO_2 ¹⁸, Co_2O_3 ¹⁹, Co_3O_4 ²⁰, In_2O_3 ²¹, $NiO/Ni(OH)_2$ ^{22,23}, binary Ni-Co hydroxide²⁴, etc.²⁵⁻²⁷ which introduce fast surface redox reactions. Previously, we reported the growth of high-quality graphene and carbon nanotube (CNT) hybrid hierarchical nanostructures grown on high porosity nickel foam via one-step ambient pressure chemical vapor deposition (APCVD)⁷. This novel few-layer graphene and CNT hybrid foam (GM) is a 3D graphene foam conformally covered with densely packed CNT networks. High performance SCs with long cycle stability had been demonstrated. However, the specific capacitance and energy density are still relatively low compared to the performance of pseudocapacitive metal oxide nanostructures. Among all pseudocapacitive materials, RuO_2 appears to be the most promising material for SCs with the following advantages: i) simple and scalable synthesis, ii) high capacitance, and iii) rapid charging-discharging. In this article, we developed a novel 3D sub-5nm hydrous RuO_2 nanoparticles anchored graphene and CNT hybrid foam (RGM) nanocomposite system, which demonstrates

superior gravimetric capacitance (502.78 F g^{-1}) and areal capacitance (1.11 F cm^{-2}) simultaneously. We integrated the 3D GM architecture²⁸ and sol-gel synthesized hydrous RuO_2 nanoparticles by a simple and scalable dip coating process, which yields a novel few-layer graphene foam architecture conformally covered with hybrid networks of RuO_2 nanoparticles and anchored CNTs. The porous GM foam not only provides a large surface area for the loading of RuO_2 nanoparticles but also facilitates electrolyte infiltration²⁹. The hybrid RGM nanocomposite network demonstrates a hierarchical and porous structure which enables enough electrolyte access to active materials. At the same time, the embedded CNTs in the CNT- RuO_2 network layer works as a conductive framework. Compare with other reported hybrid RuO_2 systems³⁰⁻³², our innovative RGM architecture offers seamless connections at the graphene and CNT interface enhances the interfacial integrity of major components (active materials and current collector) which improves the conductivity and charge transport of the whole electrode. Good electrolyte access, enhanced conductivity and improved charge transport further lead to very high active material utilization, smaller internal resistance ($\text{ESR} \sim 1 \Omega$), superior rate capability, and cycling stability³³. In addition to a very high specific capacitance compared with other previously reported pseudocapacitive systems, symmetric ECs based on this innovative RGM hybrid foam architecture could be cycled reversibly in a operational voltage window of 1.5 V, which is much larger than the majority of aqueous electrolyte supercapacitors ($\sim 1.0 \text{ V}$)^{19,33-38}. The high specific capacitance and extended operational voltage window lead to an impressive maximum energy density of 39.28 Wh kg^{-1} and power density of $128.01 \text{ kW kg}^{-1}$. In addition to the capacitance and energy density enhancement, the SC also shows an excellent cycling stability of 106% capacitance retention over 8100 cycles. The slight capacitance enhancement (6%) observed after 8100 cycles might be due to the electrochemical activation of the active material

which has also been found in GM SCs as reported previously⁷. Lastly, our RGM nanocomposite system demonstrates a binder-free technique for preparing high-energy SC electrodes^{39,40}.

Results

Figure 1a shows the microstructural illustration of the synthesis process of the sub-5nm RuO₂ nanoparticle anchored graphene and CNT hybrid foam (RGM). The GM hybrid nanostructure is grown on a nickel foam backbone via a typical one-step ambient pressure CVD process by introducing a mixture gas of H₂ and C₂H₂/C₂H₄ at 750 °C⁴¹. As indicated in our previous work, the few-layer graphene foam works as both a current collector and a buffer layer which facilitates the charge transfer from active materials to current collectors and enhances the electrochemical stability of nickel foam by insulating it from the electrolyte. In addition, the embedment of the CNTs with the graphene layer provides a seamless connection between the active material (CNT) and the current collector (few-layer graphene foam), which improves the mechanical stability of the system⁴¹. The porous GM foam serves as a perfect substrate for the loading of pseudocapacitive materials in the form of nanowires, nanoparticles and other nanostructures. Ruthenium oxide nanoparticles were synthesized according to literature with a modified sol-gel method as described in the experimental section⁴². The as grown GM foams are mildly treated with UV-generated ozone for 60 seconds to enhance the surface wettability, and this process had been verified to be a nondestructive process⁴³. X-ray diffraction (XRD) measurements were performed to confirm the phase and purity of the RuO₂ nanoparticles. The XRD pattern can be indexed as hydrous or amorphous RuO₂ nanoparticles which is in accordance with previously reported literature (Figure S1). Electron diffraction reaffirms that the

crystals are hydrous or amorphous (Figure S2b). Different from other types of pseudo-capacitive materials such as V_2O_5 , MnO_2 , and NiO , etc., hydrous and amorphous forms of RuO_2 demonstrate better capacitive ability than anhydrous RuO_2 . The higher energy density obtained by $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ is attributed to the mixed protonic-electronic conduction. The hydrous regions allow for facile proton permeation into the bulk material while the interconnected ruthenium oxide region accounts for electronic conduction^{44,45}.

The loading mass of carbonaceous material can be simply controlled with various growth conditions of the CVD process including time, catalyst amount, and carbon source concentration.⁴¹ The loading amount of RuO_2 nanoparticles can be controlled by the surface morphology, wettability of GM foam, and the dispersion concentration of the nanoparticle suspension. The loading mass in this work is the total weight of few-layer graphene, CNTs and RuO_2 nanoparticles. This was obtained by measuring the weight change of the nickel foam before and after material loading.

Scanning electron microscopy (SEM) micrographs are shown to illustrate the structural and morphological properties of the as-grown GM foam, lightly loaded RGM nanocomposites, and heavily loaded RGM nanocomposites, respectively (Figure 1b-1d). Low magnification (Figure 1b) and high magnification (Figure 1b inset) are used to show the porous 3D GM foam with densely packed and randomly oriented CNTs, which possesses a very large surface area (Langmuir and Brunauer-Emmett-Teller (BET) surface areas were found to be 743 and 497 $\text{m}^2 \text{g}^{-1}$, respectively²⁸). Figure 1c and 1d demonstrate the RGM foam with a different loading mass. High resolution (HR) TEM image demonstrates that the ultra-fine hydrous RuO_2 crystalline size is around 1-2 nm (Figure 2a and **Figure S3**). Hydrous RuO_2 nanoparticles tended to agglomerate to form larger particles after drying. Energy dispersive spectroscopy (EDS) microanalysis on a

randomly selected area of a hydrous RuO_2 sample indicates that the sample consists of Ru, O, and traceable amount of Na from the reaction precursor (Figure 2b).

X-ray photoelectron spectroscopy (XPS) characterization was performed to confirm the hydrous nature of the as-synthesized RuO_2 nanoparticles. The survey XPS spectrum from our sample is provided in Figure 3a. Although ruthenium is typically analyzed in XPS by following the strong singals from the 3d photoelectrons, here we used the 3p spectra instead in order to avoid interferences from the carbon substrates. The Ru 3p_{3/2} peak was deconvoluted into two components, which were identified with RuO_2 (462.2 eV)⁴⁶ and RuOH (464.1 eV). Those signals were found to exhibit an intensity ratio of 1 to 1.2 (Figure 3b). A similar ratio (1:1.3) is estimated from Ru-O-Ru, identified at 529.0 eV⁴⁷, and Ru-O-H, centered at 530.2 eV (Figure 3c). The XPS data in the C 1s region (Figure 3d) is quite complex, showing a total of seven components including peaks assigned to the Ru 3d photoelectrons, at 280.8 eV (Ru 3d_{5/2} of RuO_2 ⁴⁶, labeled A) and at 281.7 eV (a shake-up feature due to final state effects⁴⁸, labeled B). The peak at 283.3 eV, labeled C, was assigned to RuOH . The C 1s peak at 285.0 eV, from our support, was used for binding energy calibration; the rest of components comes from Ru 3d_{3/2} photoelectrons.

Two-electrode configuration symmetric SCs based on the RGM nanostructure foam electrodes were fabricated which includes two equal area RGM foam electrodes spaced apart by a porous separator. Cyclic voltammetry (CV) for RGM supercapacitors (SCs) were initially conducted at scanning rates between 10 mV sec⁻¹ and 200 mV sec⁻¹ in 2 M Li_2SO_4 aqueous electrolyte to estimate the capacitance and determine the useable voltage window. CV characteristics of the RGM supercapacitor with a range of various operational voltage windows at a scan rate of 50 mV s⁻¹ are shown (Figure S4). With the increasing of potential limits from

1.0 to 1.8 Volts, more RuO₂ nanoparticles are involved in the surface-redox process. It is obvious that when the voltage window is increased beyond 1.8 V, an increasing amount of irreversible charge is observed which suggests the decomposition of aqueous electrolyte with hydrogen or oxygen evolution. It is impressive to see that no significant increase of anodic current is revealed at or below 1.5 V. These results suggest that the operation of this type of RGM supercapacitor with an exceptional operational voltage window of 1.5 V is feasible which is comparable to certain asymmetric SC systems and much larger than the majority of aqueous electrolyte supercapacitors (~1.0 V) which are thermodynamically limited to a operational voltage window of 1.0 V due to the decomposition of water at 1.23 V.^{19,34-38} We believe there are four possible reasons leading to the extended operational voltage window of the RGM SC system: (i) RuO₂ electrodes are capable of working in both negative and positive voltage windows which leads to a high operational voltage window for a packaged symmetric SC cell.⁴⁹ (ii) High hydrogen and oxygen evolution overpotentials of the RGM electrodes in aqueous electrolyte due to the nanocrystalline nature of RuO₂.⁴⁹ (iii) Larger operational voltage window due to the usage of lithium sulfate aqueous solution as the electrolyte which has previously been confirmed.⁵⁰ (iv) Enhanced electrochemical stability of this innovative RGM foam architecture.⁵¹ Figure 4a shows the near rectangular CV characteristics of the 3D RGM hybrid nanostructure foam with a potential window of 1.5 V under different scan rates. The nearly rectangular shape and the absence of oxidation and reduction peaks are observed for all scan rates suggesting that SCs based on RGM electrodes have small equivalent series resistance, high rate capability, and excellent electrochemical performance. Moreover, the nearly mirror-image shape of CV curves indicate exceptional reversibility and a very fast surface reaction.⁵² The nearly identical specific capacitance characteristics for all scan rates further indicate outstanding process stability,

repeatability, and superior performance of the SC.⁵³⁻⁵⁵ Chronopotentiometry measurements were also conducted with a large operation voltage window of 1.5 V to further evaluate the electrochemical performance of the RGM foam supercapacitors. Charge-discharge (CC) characteristics with different current densities are shown in Figure 4b. The near linear and symmetric charge and discharge curves suggest an excellent capacitive performance with a rapid I-V response for our device. The calculated specific capacitances under different current densities below 200 mA cm⁻² are shown in Figure 4c. The highest gravimetric capacitance of 502.78 F g⁻¹ and areal capacitance of 1.11 F cm⁻² were obtained at the same time under a current density of 1 mA cm⁻². Normally two mechanisms are involved in the storage of charges in the carbonaceous and pseudo-capacitive material hybrid electrodes⁵⁶.

Long cycling life is also one of the most critical factors for the application of supercapacitor electrodes. A sequence of charge-discharge cycles for our RGM nanostructure foam (Voltage window 1.5 V) and one control sample (Voltage window 1.0 V), which was based on RuO₂ nanoparticles on pristine nickel foam and GM foam under the current density of 96 mA cm⁻² (Figure 4d). After 8100 cycles, superior capacitance retention (~106%) was maintained for the RGM nanostructure. The control sample was prepared via mixing hydrous RuO₂ nanoparticles with 2% PVDF binder in NMP as the solvent. The slightly enhanced capacitance (6%) observed after 8000 cycles might be due to the electrochemical activation of the active materials during cycling. The slight capacitance enhancement (~6%) of the RGM device via cycling could also be due to the increased effective interfacial area between the RGM foam structure and the electrolyte with an increase in reaction time^{35,57}. This self-strengthening effect also helps to stabilize the device during long term operation. We believe this binder-free design

of oxide anchored nanocarbon hybrid supercapacitor architecture is promising for future energy storage applications.

Potentiostatic electrochemical impedance spectroscopy (EIS) measurements were performed to further characterize the performance of RGM SCs. Potentiostats are required to run impedance tests in a linear regime, so that test results remain consistent throughout⁵⁸. The Nyquist plots obtained via EIS show that the RGM SC behaves approximately like an ideal supercapacitor in the low frequency region. This can be seen in both plots in Figure 4e (1st cycle and after 8100th cycle), where they show a near linear and vertical characteristic in this region^{59,60}. Some deviation from absolute ideality is evident in a large but finite slope of the plot in this region. This can be a result of frequency dispersion due to wider distribution of the pore size of the porous matrix.⁶¹

The equivalent circuit used for fitting of the EIS plots in this work is shown in Figure 5a. The EIS plots are fitted according to the model, and the as-fitted EIS plots are shown in Figure 5b-c. The fitted data for all circuit elements are shown in Table 1. R_s (also known as the solution resistance) is the equivalent series resistance (ESR), which generally describes the resistance of the electrolyte combined with the internal resistance of the electrode⁶². EIS plots after the 1st cycle and 8100th cycle were obtained to evaluate the internal resistance change during charge-discharge cycling (Figure 4e). Both spectra possess a low ESR of approximately 1.5 Ω , which further demonstrate an exceptional electrochemical cycling stability of our hybrid nanostructure foam electrodes. This is evident as the nearly rectangular shape of the CV curves (Figure 4a) is maintained even in very high scan rates⁶³. The decreased ESR (Table 1) from 1.7 ohm to 1.52 ohm after 8100 cycles may correspond to a reduction in internal resistance of the electrodes due to the electrochemical activation of active materials during cycling. R_{CT} (also known as charge

transfer resistance) characterizes the rate of redox reactions at the electrode-electrolyte interface⁶⁴. The charge transfer resistance dictates the speed of ion transport through the electrode-electrolyte interface⁶⁵. We believe another factor contributing to the excellent cycling performance of RGM nanostructure foam system is the graphene layer facilitating charge transfer between the RuO₂ anchored CNT network layer and the current collector (nickel foam). Additionally, the resultant relatively small charge transfer resistance should be associated with increased contact area at the electrode-electrolyte interface⁶⁶. Thus, ion transfer and charge transfer is easily facilitated and reversibility is improved. CPE_{DL} is the constant phase element (CPE) representing double layer, which occurs at interfaces between solids and ionic solutions due to separation of ionic and/or electronic charges⁶². As shown in Table 1, the CPE_{DL} increases with cycling. This is due to activation of more material and the corresponding increase in surface area available as the supercapacitor was cycled repeatedly which is in accordance with the enhanced capacitance retention observed in Figure 4d. This hypothesis is also supported by the observed drop in R_{CT} after 8100 cycles. The double layer capacitance increased by ~1000% while charge transfer resistance decreased by ~80% after the RGM supercapacitor was cycled 8100 times. W_0 is the Warburg element, which represents the diffusion of ions into the porous electrode during the intermediate frequency region⁶⁷. The slope of the Warburg region dictates electric double layer forming speed⁶⁸. As the slope is increased, the speed of formation of the double layer is also increased. Additionally, a possible reason to insensitivity to varying voltage scan rates is a short and equal diffusion path length of the ions in the electrolyte, as evidenced by a short Warburg region on the Nyquist plots⁶⁹. R_L is the leakage resistance which is placed in parallel with CPE_L ⁶⁷. This is usually very high and can be ignored in the circuit. CPE_L denotes

pseudocapacitance, which arises with voltage dependent Faradaic charge transfer processes. No significant change in pseudocapacitance is observed in RGM system before and after cycling⁶².

Plots of normalized real capacitance and imaginary capacitance against frequency for pristine RGM, and RGM after 8100 cycles are shown in Figure 5d and 5e. It can be observed that the RGM system after cycling shows a higher capacitive and less resistive behavior than the pristine RGM system. The RGM system after 8100 cycles shows a faster dielectric relaxation time characteristic⁶⁶ than that in its pristine form. Therefore, ion diffusion is further facilitated with increasing cycling numbers for the RGM system. All of these results support our claim of superior stability of the as-prepared RGM system.

In normalized real capacitance vs. frequency plot for the RGM system after 8100 cycles (Figure 5d), we observe that the capacitance remains invariant for a larger frequency region. This is desirable and is indicative of ideal supercapacitive behavior⁹. Stability is more desirable than improvement in supercapacitor performance over a number of cycles. However, both stability and improvement are more desirable than deteriorating performance. The RGM system shows stability with minimal improvement with increasing cycling number. It does not show deterioration of capacity or of charge/discharge rate (dictated by dielectric relaxation time characteristic) after being cycled 8100 times.

The EIS plots of GM, RGM, and a control sample made from RuO₂ nanoparticles only are shown to further characterize the excellent performance of our RGM system (Figure 6a, 6b). Although the anchoring of the sub-5nm hydrous RuO₂ nanoparticles to the GM foam introduced a slight increase of ESR from 1.253 ohm to 1.7 ohm (Figure 6b), compared to the control samples based on nickel/RuO₂ electrode (ESR~3.13 ohm), a much lower ESR is achieved with our RGM system(~46 % decrease).

Discussion

To further evaluate the performance of the RGM foam for SC electrodes, we calculated the energy density (E) and power density (P) based on the chronopotentiometry measurements of our devices. The SC based on RGM hybrid electrodes exhibits a high energy density of 39.28 Wh kg⁻¹ at 0.356 kW kg⁻¹ which gradually reduces to 18.49 Wh kg⁻¹ at 128.01 kW kg⁻¹ (Table S1).. Figure 6c shows a Ragone plot indicating energy density (E) versus power density (P) values of packaged RGM SC and GM SC⁷ in detail which suggest this innovative RGM SC comparatively superior in performance compared to other types of RuO₂ or C-RuO₂ hybrid electrochemical capacitor systems^{31,41,70,71}. The indicated E and P values are based on the mass of the active materials of the electrodes. Because the active material normally takes about ~1/3 of the total mass of the packaged commercial supercapacitors, the energy density or power density is frequently estimated to be the ~1/3 of the electrode material^{72,73}. The maximum energy density of 13.09 Wh kg⁻¹ and the highest power density of 42.67 kW kg⁻¹ in aqueous electrolyte for packaged RGM SC are still comparable to other types of electrochemical capacitor systems^{1,31,41,70-72}. These results suggests that our hybrid nanostructure foam is an exceptional candidate for future electrochemical capacitor and battery electrodes.

In summary, a novel 3D RGM foam has been demonstrated. This 3D RGM foam was prepared by ambient pressure chemical vapor deposition of graphene and CNT foam structure and simple bath deposition of sub-5nm hydrous RuO₂ nanoparticles. This method of preparing electrodes is a facile and scalable approach for high energy density supercapacitor applications. The two-step process successfully integrates the conformal coating of pseudocapacitive nanoparticles on the GM backbone to form an interpenetrated network between CNTs and

hydrous RuO₂ nanoparticles which shown exceptional capacitive ability and high conductivity. The RGM electrode shows superior gravimetric and per-area capacitive performance (specific capacitance: 502.78 F g⁻¹, areal capacitance: 1.11 F cm⁻²) at the same time. The high specific/areal capacitance and extended operational voltage window of 1.5 V lead to an exceptionally high energy density of 39.28 Wh kg⁻¹ and power density of 128.01 kW kg⁻¹. In addition to the capacitance and energy density enhancement, the RGM SC also shows an excellent cycling stability of ~106% capacitance retention over 8100 cycles. The electrochemical stability, excellent capacitive performance, and the easiness of the preparation method suggest this unique material system is promising for future high performance energy storage applications.

Methods

Materials synthesis. Graphene and CNTs foam was grown via a chemical vapor deposition (CVD) process by introducing a mixture of hydrocarbon (C₂H₄/C₂H₂) and hydrogen on 0.5 mm thick nickel foam⁷. A mild reactive ion etching (RIE) O₂-plasma is applied to nickel foam and 1-5 nm Fe catalysts are deposited by e-beam evaporation (Temescal, BJD-1800). The treated Ni foam is heated to 750 °C, and hydrocarbon gas is introduced to trigger and continue the growth of graphene and CNTs synchronously on the nickel foam frame. Hydrous RuO₂ was synthesized according to literature with a modified sol-gel method.⁴² In brief, NaOH solution (1M) was slowly injected slowly into 100 ml RuCl₃ (0.1 M, Sigma Aldrich, USA) by a micro fluid system at a rate of 0.5 cm³ min⁻¹ to balance the PH to 7. $RuCl_3 + 3NaOH = Ru(OH)_3 + 3NaCl$. The mixed solution was stirred for another 12 hours, then centrifuged and washed with de-ionized (D.

I.) water several times to remove the unwanted residual salts (NaCl). Next, the sample was vacuum dried at 120 °C for 12 hours. The as-prepared hydrous RuO₂ nanoparticles were dispersed in D.I. water again to form slurry like solution. The as-grown GM was treated with UV generated ozone for 60 seconds, and then it was dipped into the RuO₂ slurry to load the RuO₂ nanoparticles. After dip-coating, the hybrid RGM foam was dried and annealed at 150 °C for 6 hours under vacuum. The as-synthesized RuO₂ nanoparticles were dispersed in D.I. water with an ultrasonic treatment to form a uniform gel-like suspension (concentration ~5 mg ml⁻¹). The resulting suspension was kept stirring. The as-synthesized hydrous RuO₂ nanoparticles were incorporated into the GM foam structure by a simple dip coating process in the RuO₂ nanoparticles suspension. The sol-gel synthesized hydrous RuO₂ nanoparticles and GM foam exhibit intimate interfaces due to abundance of hydrophilic groups on their surface, which yields an ultra-fine hydrous RuO₂ nanoparticles coated CNT network layer on graphene foam after vacuum drying.

Materials characterization. The surface morphology is investigated using optical microscopy, scanning electron microscopy (SEM; leo-supra, 1550) with an X-ray energy-dispersive spectroscopy (EDS), and transmission electron microscopy (TEM; Philips, CM300) with a LaB₆ cathode operated at 300 KV. The TEM samples were prepared by dispersing the as prepared RuO₂ nanoparticles in ethanol and then coating the dispersed nanoparticles onto carbon film coated TEM grid by simply dropping. X-ray photoelectron spectroscopy (XPS) characterization of the samples was carried out by using a Kratos AXIS Ultra DLD XPS system equipped with an Al K α monochromated X-ray source and a 165-mm mean radius electron energy hemispherical

analyzer. All binding energies were calibrated in reference to a value of 285.0 eV for the C 1s peak.

Fabrication and measurements of supercapacitor cells. A symmetrical packaged supercapacitor configuration was employed for the electrochemical measurements, where the two as-prepared RGM foams are assembled into a sandwich structure with a porous membrane (Celgard 3501), which functions as a separator in-between. In this work, an aqueous electrolyte (2 M Li₂SO₄) is used. Cyclic voltammetry (CV), chronopotentiometry (charge-discharge (CD)), and electrochemical impedance spectroscopy (EIS) were conducted to evaluate the performance of the supercapacitors. Potentiostatic EIS measurements were performed between 0.1Hz and 1MHz with amplitude of 10 mV. Specific capacitance C_s values are calculated from the charge-discharge curves via equation (1) $C_s = 2i/m(dV/dt)$. Where m is the mass of active material for one electrode, i is the discharge current and dV/dt is the slope of the discharge curve. The energy density (E) and power density (P) of the whole cell are calculated by using $E = 0.5C(\Delta V)^2$, and $P = E/t$, where t is the total time of discharge. C is the specific capacitance value of the supercapacitor cell which is equal to $0.25 C_s$, and ΔV is the potential range.

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Author Contributions

W.W., S. G., M.O. and C.S.O. designed the experiments and wrote the main manuscript. W.W., S.G. and J.Z. worked on materials synthesis, supercapacitor fabrication, galvanostatic charge-

discharge measurements, cyclic stability tests, and electrochemical impedance spectroscopy (EIS) measurements. K.A. performed equivalent circuit fitting. I. L. and F. Z. performed XPS analysis. C.S.O. managed the research team. All authors reviewed the manuscript.

Additional Information

The author(s) declare no competing financial interests.

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Legends

Figure 1. Microstructure of RGM electrode. (a-b) Schematic illustration of the preparation process of RGM nanostructure foam. SEM images of (c) as-grown GM foam (d) Lightly loaded RGM, and (e) heavily loaded RGM.

Figure 2. (a) HRTEM image of RuO₂ nanoparticles. (b) EDS spectrum of the RuO₂ nanoparticles showing the presence of the main components Ru, O along with minor amounts of sodium. Cu and C peak are background from the TEM support grid.

Figure 3. (a) Survey, (b) Ru 3p, (c) O 1s, and (d) Ru 3d XPS spectra of hydrous RuO₂.

Figure 4. Electrochemical performance of the supercapacitor based on RGM electrode. (a) Cyclic voltammetry measurements for RGM SC performed under different scan rates of 10, 20, 50, 100 and 200 mV s⁻¹. (b) Galvanostatic charge-discharge curves of a RGM SC at different current densities. (c) Specific capacitance and per-area capacitance of a RGM SC obtained from CC curves at different current densities. (d) Cyclic stability test of the RGM SC at the current density of 96 mA cm⁻². Data from control samples of pure RuO₂ nanoparticles are shown for comparison. (e) Plots of the potentiostatic electrochemical impedance spectroscopy (EIS) measurements conducted between 100 mHz and 1 MHz with an amplitude of 10 mV after 1st and 8100th cycle respectively.

Figure 5. Electrochemical Impedance Spectroscopy (EIS) study. (a) The equivalent circuit of Randle's model, where R_s is the equivalent series resistance (ESR), R_{CT} is the resistance of the electrode-electrolyte, R_L is the leakage resistance. CPE_{DL} is the constant phase element (CPE) of double layer, $W0$ is the Warburg element, CPE_L is the mass capacitance. Experimental and modeled Nyquist plots for complex impedance for RGM after (b) 1st cycle and (c) 8100th cycle. (d) Normalized real capacitance against frequency plot and (e) normalized imaginary capacitance against frequency for RGM, and RGM after 8100 cycles.

Figure 6. (a) EIS plots and (b) high frequency region EIS plots of GM, RGM, a control sample (RuO₂ nanoparticles only), respectively. (c) Ragone plot related to energy densities and power densities of the packaged whole cell RGM SC, GM SC⁷, RuO₂ nanoparticles SC³¹, hydrous ruthenium oxide (RuO₂)/graphene sheets composite (GOGSC)³¹, RuO₂ nanowire/single walled carbon nanotube (SWNT) hybrid film⁷⁰.

Table 1. Fitted equivalent circuit elements of RGM before and after cycling.

Table 1

RGM	R_s	R_{CT}	CPE_{DL}	W_O	CPE_L	R_L
1st	1.7 Ω	1.02 Ω	Q _{DL} =0.00095 n _{DL} =0.635	W _{OR} =2.5 W _{OC} =0.42	Q _L =0.16 n _L =0.75	2000 Ω
8100th	1.524 Ω	0.195 Ω	Q _{DL} =0.011 n _{DL} =0.65	W _{OR} =3 W _{OC} =0.5	Q _L =0.13 n _L =0.83	2000 Ω











